I. HYDROGEN BONDING OF INORGANIC OXYCHLORIDES

II. PREPARATION, PROPERTIES, AND REACTIONS OF THE PHOSPHONITRILIC CHLORIDES

BY

ROBERT STEINMAN

B.S., Carnegie Institute of Technology, 1939
M.S., University of Illinois, 1940

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL
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URBANA, ILLINOIS
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I. HYDROGEN BONDING OF INORGANIC OXYCHLORIDES

Considerable work has been done on the donor ability of oxygen and nitrogen containing organic compounds with potential acceptor solvents. However the donor ability of inorganic compounds, specifically the inorganic acid chlorides, with compounds containing an acceptor hydrogen to form the C-H←O linkage had not yet been investigated. In order to evaluate the influence of the highly negative chlorine atoms in the acid chlorides, it also became necessary to compare the observed effects with those of certain related organic compounds. The experimental study involved the determination of the heats of mixing of phosphoryl chloride, sulfuryl chloride, thionyl chloride, diethyl carbonate, diethyl sulfite, diethyl sulfate, and propionyl chloride with chloroform and with carbon tetrachloride according to the method described by Zellhoefer and Copley.[2]

The high heats of mixing of the inorganic acid chlorides with chloroform as acceptor solvent, in comparison to the negligible heat effects observed upon mixing the same compound with carbon tetrachloride, give definite evidence of hydrogen bonding. The influence of the chlorine atoms in decreasing the donor ability of the semi-polar oxygen atoms in forming hydrogen bonds was verified by substituting ethoxy groups for the chlorine atoms. Higher heats of mixing with chloroform were observed in the case of the esters than with the corresponding acid chlorides. This substantiates the postulate of Glasstone[1] that the electron attracting nature of the chlorine atoms decreases the donor ability of the oxygen atom.

1. Glasstone, Trans. Faraday Soc., **33**, 200 (1937).
2. Zellhoefer and Copley, J. Am. Chem. Soc., **60**, 1343 (1938).

II. PREPARATION, PROPERTIES, AND REACTIONS OF THE PHOSPHONITRILIC CHLORIDES

A. Preparation

The Schenck and Romer[1] method of preparing the phosphonitrilic chlorides by heating phosphorus pentachloride with ammonium chloride in s-tetrachloroethane, although the best so far devised, has several distinct disadvantages. Each preparation requires a) twenty to twenty-four hours of refluxing, b) the removal of the solvent by vacuum distillation, and c) washing with benzene to remove the oily polyhomologs. A simple and rapid method of preparation of the phosphonitrilic chlorides has been devised by the author and involves heating an intimate mixture of phosphorus pentachloride and excess ammonium chloride at temperatures between 130-150°C. The reaction proceeds in accordance with the equation

$$PCl_5 + NH_4Cl = (PNCl_2)x + 4HCl$$

where x = 3, 4, and higher polyhomologs. The trimer and tetramer are selectively extracted with petroleum ether; the oily homologs, by benzene, chloroform or carbon tetrachloride.

Phosphonitrilic chloride is not formed when phosphorus pentachloride and triphosphorus pentanitride are heated up to temperatures of 225°C.

B. Separation

A successful separation of trimeric from tetrameric phosphonitrilic chloride can be achieved only by a process involving fractional vacuum distillation, followed by crystallization and sublimation. The vacuum distillation results in trimer and tetramer rich fractions; the crystallization from 100 percent acetic acid gives products pure enough for chemical purposes; but only sublimation under reduced pressure yields products suitable for physico-chemical measurements.

1. Schenck and Romer, Ber. **57B**, 1343 (1924).

C. Ammonolysis

Ammonolysis of the trimeric and tetrameric phosphonitrilic chlorides with liquid ammonia results in the formation of the respective phosphonitrilamides. Deammonation of these amides appears to be irreversible and takes place progressively at temperatures up to 230°C. The rate of deammonation increases with temperature; no apparent difference in the rates of deammonation of the trimeric and tetrameric phosphonitrilamides could be observed. The products are ammonia and presumably phospham.

$[PN(NH_2)_2]_x = (PNNH)_y + NH_3$ where x = 3, or 4 and y = higher polymers(?). No evidence was obtained for the formation of stable intermediate products.

D. Aminolysis

With primary and secondary amines, the phosphonitrilic chlorides may undergo aminolysis directly, in solution, or in pyridine, and rather definite compounds are obtained. The N-substituted phosphonitrilamides of the aliphatic and cycloaliphatic amines appear to be varied in nature for duplicate analyses of the same compounds never agreed. This may possibly be due to the difficulty in replacing all the chlorine atoms with the amine groups, or to the formation of a very stable phosphorus-nitrogen derivative which is not decomposed during analysis. Reactions of the trimeric and tetrameric phosphonitrilic chlorides and of the polymeric elastomer were carried out using the following amines: aniline, cyclohexylamine, dicyclohexylamine, n-octylamine, n-hexylamine, diethylamine, n-isobutylamine, and n-butylamine.

E. Vapor Pressure

The apparatus and method employed in measuring the vapor pressures of trimeric phosphonitrilic chloride were those previously employed by Laubengayer and Schirmer.[2]

On the basis of measured values the change in vapor

2. Laubengayer and Schirmer, J. Am. Chem. Soc., **62**, 1578 (1940).

pressure of the solid with respect to temperature may be represented by the equation

$$\log p = 11.1869 - 3.9776(1/T)$$

The vapor pressure of the liquid trimer over the temperature range 114° (the melting point) to 190° is given by the equation

$$\log p = 8.3568 - 2.8796(1/T)$$

The melting point of trimeric phosphonitrilic chloride as calculated from the intersection of these equations is 114.9°. This agrees well with the value 114° reported by other investigators.[1,3] The boiling point obtained by extrapolation of the liquid-vapor curve to 760 mm. pressure is 252.7°, and is in fair agreement with the value 256° reported by Stokes.[3]

The molar heat of vaporization calculated from the slope of the liquid-vapor curve is 13.17 kilocalories. The molar heat of sublimation calculated from the slope of the solid-vapor curve is 18.20 kilocalories, and the molar heat of fusion obtained by difference is 5.03 kilocalories.

3. Stokes, Am. Chem. J., **19**, 782, (1897).

VITA

The writer was born in New York City on March 30, 1918. He attended the public schools of Pittsburgh, Pennsylvania and was graduated from Schenley High School in June, 1935. In the fall of that year he entered the Carnegie Institute of Tecnnology and was graduated as thirteenth honor student with a Bachelor of Science degree in Chemistry in June 1939. During his undergraduate work he held a Carnegie Institute of Technology Scholarship and a Buhl Foundation Scholarship.

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